

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION  
International Bureau



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification <sup>6</sup> :	A1	(11) International Publication Number: WO 96/21752
C23C 22/34		(43) International Publication Date: 18 July 1996 (18.07.96)
(21) International Application Number:	PCT/US96/00517	(81) Designated States: AL, AM, AU, BB, BG, BR, CA, CN, CZ, EE, FI, GE, HU, IS, JP, KG, KP, KR, LK, LR, LT, LV, MD, MG, MK, MN, MX, NO, NZ, PL, RO, SG, SI, SK, TR, TT, UA, UZ, VN, ARIPO patent (KE, LS, MW, SD, SZ, UG), Eurasian patent (AZ, BY, KZ, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).
(22) International Filing Date:	11 January 1996 (11.01.96)	
(30) Priority Data:	08/370,323 10 January 1995 (10.01.95) US	
(71) Applicant:	CIRCLE-PROSCO, INC. [US/US]; 2017 Yost Avenue, Bloomington, IN 47403 (US).	Published <i>With international search report.</i>
(72) Inventors:	TOMLINSON, Charles, E.; 970 Conservation Club Road, Martinsville, IN 46151 (US). MUEHL, Thomas, P.; 9141 West Fenceline Road, Spencer, IN 47460 (US). PARKER, Douglas, K.; 2331 Linden Hill Road, Bloomington, IN 47401 (US). MORTON, William, H.; 4809 Andover Court, Bloomington, IN 47404 (US).	
(74) Agents:	THOMAS, Timothy, N. et al.; Woodard, Emhardt, Naughton, Moriarty & McNett, Bank One Center/Tower, Suite 3700, 111 Monument Circle, Indianapolis, IN 46204 (US).	

(54) Title: A PROCESS OF COATING METAL SURFACES TO PRODUCE A HIGHLY HYDROPHILIC, HIGHLY CORROSION RESISTANT SURFACE WITH BIORESISTANCE AND LOW ODOR IMPACT CHARACTERISTICS

(57) Abstract

A chromium-free process for providing a metal surface with the properties of corrosion resistance, hydrophilicity, low odor and bioresistance. The process includes initially treating the metal with a solution of fluoride, zirconium and a protic acid. Then, the metal is treated with a solution of water-soluble silicate at an alkaline pH. Rinses are optionally used after each stage, and an oven drying stage is preferred as the final step in the process.

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AM	Armenia	GB	United Kingdom	MW	Malawi
AT	Austria	GE	Georgia	MX	Mexico
AU	Australia	GN	Guinea	NE	Niger
BB	Barbados	GR	Greece	NL	Netherlands
BE	Belgium	HU	Hungary	NO	Norway
BF	Burkina Faso	IE	Ireland	NZ	New Zealand
BG	Bulgaria	IT	Italy	PL	Poland
BJ	Benin	JP	Japan	PT	Portugal
BR	Brazil	KE	Kenya	RO	Romania
BY	Belarus	KG	Kyrgyzstan	RU	Russian Federation
CA	Canada	KP	Democratic People's Republic of Korea	SD	Sudan
CF	Central African Republic	KR	Republic of Korea	SE	Sweden
CG	Congo	KZ	Kazakhstan	SG	Singapore
CH	Switzerland	LI	Liechtenstein	SI	Slovenia
CI	Côte d'Ivoire	LK	Sri Lanka	SK	Slovakia
CM	Cameroon	LR	Liberia	SN	Senegal
CN	China	LT	Lithuania	SZ	Swaziland
CS	Czechoslovakia	LU	Luxembourg	TD	Chad
CZ	Czech Republic	LV	Latvia	TG	Togo
DE	Germany	MC	Monaco	TJ	Tajikistan
DK	Denmark	MD	Republic of Moldova	TT	Trinidad and Tobago
EE	Estonia	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	UG	Uganda
FI	Finland	MN	Mongolia	US	United States of America
FR	France	MR	Mauritania	UZ	Uzbekistan
GA	Gabon			VN	Viet Nam

**A PROCESS OF COATING METAL SURFACES TO PRODUCE A HIGHLY HYDROPHILIC, HIGHLY CORROSION RESISTANT SURFACE WITH BIORESISTANCE AND LOW ODOR IMPACT CHARACTERISTICS**

**FIELD OF THE INVENTION**

5       The present invention relates generally to corrosion resistant coatings for metal surfaces, and more particularly to low-odor, bioresistant, hydrophilic, corrosion resistant coatings for aluminum.

**BACKGROUND OF THE INVENTION**

10     The present application is a continuation-in-part of applicant's copending patent application Serial No. 08/137,583, issued as U.S. Patent No. 5,380,374, which is incorporated herein by reference.

15     A variety of coatings for aluminum are known to the art. These coatings typically provide corrosion resistance to the metal, while often simultaneously providing improved paint or other organic coating adhesion.

20     Although most early coatings for metals such as aluminum were chromate-based compositions, chromate-free coatings have recently been developed. These coatings are particularly useful for applications such as coating aluminum food or beverage cans, where it is particularly desirable to avoid potentially toxic chromium.

25     Chromate-free conversion coatings often employ a Group IVA metal such as titanium, zirconium or hafnium, a source

-2-

of flouride ion and nitric acid for pH adjustment. These chromate-free conversion coatings are often clear and are used to prevent the blackening that normally occurs when aluminum is boiled in water during pasteurization.

5 For example, U.S. Patent No. 3,964,936 to Das discloses the use of zirconium, flouride, nitric acid and boron to produce a conversion coating for aluminum. U.S. Patent No. 4,148,670 to Kelly discloses a conversion coating comprising zirconium, fluoride and phosphate. U.S. Patent No. 4,273,592  
10 to Kelly discloses a coating comprising zirconium, flouride and a C<sub>1-7</sub> polyhydroxy compound, wherein the composition is essentially free of phosphate and boron. U.S. Patent No. 4,277,292 to Tupper discloses a coating comprising zirconium, flouride and a soluble vegetable tannin.

15 U.S. Patent No. 4,338,140 to Reghi discloses a conversion coating comprising zirconium, fluoride, vegetable tannin and phosphate, and optionally including a sequestering agent to complex hard water salts such as calcium, magnesium and iron. U.S. Patent No. 4,470,853 to Das et al. discloses a  
20 coating comprising zirconium, fluoride, vegetable tannin, phosphate and zinc. U.S. Patent No. 4,786,336 to Schoener et al. discloses a coating comprising zirconium, fluoride and a dissolved silicate, while U.S. Patent No. 4,992,116 to Hallman discloses a conversion coating comprising a  
25 fluoroacid of zirconium and a polyalkenyl phenol.

It should be noted that the conversion coatings of the prior art have not proven particularly effective for certain applications. In particular, the prior art has not disclosed a process for coating automotive heat exchangers so that the  
30 surface obtained is not only corrosion resistant, but is also hydrophilic, bioresistant and odor-free. These properties are particularly desired in applications such as the production of air conditioning evaporators for automobiles.

For example, U.S. Patent No. 5,234,714 to Rasso is  
35 related to a coating system using a chromate/silicate process

-3-

for "providing an aluminum heat exchanger with a corrosive-resistant hydrophilic coating." Additionally, it is stated the chemical concentrations "are precisely controlled in order to avoid producing a coating which emits 5 a musty odor." The patent describes a process wherein a "cleaning stage" [this is actually a deoxidation treatment in the described process], a "chromating" stage, and a "silicate" stage are employed.

U.S. Patent Nos. 3,762,178 and 4,672,816 to Yamamada and 10 Takahashi, respectively, deal with systems to reduce or eliminate "musty" odor from auto air conditioning systems through use of antibiological agents.

U.S. Patent No. 5,203,402 to Nishishita describes a heat exchanger design along with an organic-based coating to 15 produce a hydrophilic layer. The coating is composed of a colloidal silica suspended in an organic matrix. The suspension is cured and the "silanol groups of the colloidal silica are chemically combined with part of hydroxyl groups of the resin," reportedly resulting in a change of properties 20 of the silica and "making smells less liable to attach to the colloidal silica."

U.S. Patent No. 5,201,119 to Minzuno describes design of a heat exchanger with use of two separate coating systems. The first typically incorporating a chromium containing 25 conversion coating for corrosion protection and the second coating incorporating an antimicrobial agent [specifically, 2,2'-dithiobis(pyridine-1-oxide)] to prevent microbial growth.

Canadian Pat. Appl. No. 2083454 AA 9, Int'l. Cl. C23C-022/37 to Melzer describes a method for coating aluminum 30 and aluminum containing metals with a "no-rinse coating" for increased corrosion protection. The process described details the use of aqueous solutions of "multivalent chromium compounds comprising including in said aqueous solution a fluoride containing compound." The compositions which may be 35 used are described in U.S. Patent Nos. 4,475,957 and

-4-

4,921,552 to Sander, et al, and others so listed in the application. The process and compositions described render a surface protected by a polymer (such as a "poly(alkyleneoxy)-" type) with a multivalent transition metal incorporated into the matrix.

U.S. Patent No. 4,338,140 to Reghi is related to coating metal for improved corrosion resistance with solutions containing zirconium, fluoride and tannin compounds at pH values from 2.0 to 3.5. U.S. Patent No. 4,470,853 to Das is related to a coating composition comprised of zirconium, fluoride, tannin, phosphate, and zinc in the pH range of 2.3 to 2.95. U.S. Patent No. 5,380,374 to Tomlinson describes compositions combining Group IV-B with Group II-A elements for producing corrosion resistant coatings on metals.

U.S. Pat. Appl. No. 08/138,136 to Tomlinson describes compositions for combining Group IV-B with Group IA elements for producing hydrophilic, corrosion resistant coatings on metals in low pH and high speed applications.

The above patents do not describe the process as described below for providing a Group IV-B/silicate coating, nor is it obvious that the invention described below would produce a coating with all the desired properties. A need therefore exists for a process of coating aluminum so that the surface obtained is not only corrosion resistant but is also hydrophilic, bioresistant and odor-free. The present invention addresses that need.

-5-

#### SUMMARY OF THE INVENTION

Briefly describing one aspect of the invention, there is provided a process for improving the corrosion resistance of metal surfaces by treating the metal with a solution of fluoride, zirconium and a protic acid, subsequently treating said metal surface with a solution of water-soluble silicate at an alkaline pH, and then drying the metal surface.

One object of the present invention is to provide coatings for aluminum that are corrosion resistant, hydrophilic, bioresistant and odor-free.

Further objects and advantages of the present invention will be apparent from the following description.

-6-

#### DESCRIPTION OF THE PREFERRED EMBODIMENT

For the purposes of promoting an understanding of the principles of the invention, reference will now be made to preferred embodiments and specific language will be used to describe the same. It will nevertheless be understood that no limitation of the scope of the invention is thereby intended, such alterations and further modifications in the disclosed embodiments, and such further applications of the principles of the invention as illustrated therein, being contemplated as would normally occur to one skilled in the art to which the invention pertains.

As previously indicated, the present invention relates to a process for producing a chromium-free, highly corrosion resistant coating on the surface of a metal substrate. The chemical compositions used in the process produce a hydrophilic, corrosion resistant coating on iron, aluminum and magnesium alloys.

The invention incorporates at least three process stages. The first stage is a Group IV/mixed oxide treatment with no or minimal etching of the surface. The second is a silicate deposition stage with, for example, sodium and/or potassium silicate being suitable here. The third stage is a final "drying" stage, preferably at elevated temperature. It is during this final drying stage that metal-oxide-Group IV metal-oxide-silicate/siloxyl linkages are fully established.

The following discussion and examples will address treatment of aluminum alloys in general and aluminum alloy heat exchange units specifically. The treatments so described are applicable to ferrous, zinc, and magnesium alloys as well as aluminum.

Depending upon the final requirements of the coating, a multiplicity of stages may be used prior to those indicated above. For example, when using an aluminum substrate where

-7-

hydrophilicity of the surface is highly desirable (such as an air conditioning evaporator) a first stage prior to those listed above can incorporate components to mildly etch the oxide and simultaneously deposit mixed metal/nonmetal salts 5 (such as a Zr/K/Al/F matrix). The surfaces so obtained will provide the base layer for the three stages described in the above, rather than the natural metal oxide that exists on the base alloys. The resultant coating when all stages have been used will be slightly roughened and have many hydrophilic 10 components to provide a superior water-break-free surface. A specific example of this is presented below.

If corrosion resistance is desired above what is provided by the three required stages, a pretreatment stage may be used wherein elements or compounds are deposited to enhance 15 this inherent characteristic. For example, it has been seen that nonetching "pretreatments" in mixed Group IV/Group II/[borate, silicate, and/or phosphate] solutions may be beneficial in this regard. Also, creating a thick and uniform oxide layer by standard anodization processes 20 generally increases corrosion resistance as the coating coats this "built" oxide.

It is to be appreciated that the coatings obtained by the disclosed process are "non-nutrient" and have essentially no odor impact. These are consequences of the inorganic nature 25 of the coating obtained, and will also be inherent to each variant described when no organic component is used to supplement any characteristics of the coating system. The coating does not contain components that microorganisms use for metabolism and therefore does not promote this type of 30 growth.

It is also to be noted that borates have been shown to exhibit bioinhibition in certain environments, and in the coatings herein described where boric acid and/or polyborates have been used bioinhibition has been demonstrated.

35 Finally, it is to be appreciated that the absence of any

-8-

significant long-term odor impact is believed to be due to the lack of promotion of biological growth on these types of systems. The lack of short-term odor impact is likely due to the tightly bound and relatively neutral (with regard to 5 oxidation potential against carbonaceous components in the air stream) outer siloxyl surface obtained in this process. The lack of short-term odor impact is believed to be inherent to the process, so that only the "long-term" odor impact is significantly augmented by the use of bioinhibitory 10 components in or on the final surface.

The aqueous stages are generally at elevated temperature (>70°F) and exposure times usually run from 30 seconds to 5 minutes per stage. A notable exception would include when a "hydrophilic pretreatment" is used as described above. This 15 has been done down to 50°F [pretreatment - K/Zr/Al/F/HNO<sub>3</sub> system] with excellent results as etching is moderate and a heavy deposition of salts is obtained. Superior corrosion resistance is obtained quickly after the three primary stages (generally 30 seconds per aqueous stage) and extended 20 exposures are usually not required.

One or more rinse stages can be used sequentially following any stage. There often is a more pronounced need for rinsing with parts such as heat exchange units that are complicated geometrically. Fresh water is continuously 25 introduced to the rinse baths to maintain cleanliness. Manual or automatic monitoring of pH or conductivity can be used to determine and maintain cleanliness of the rinse stages.

A deionized water rinse stage is preferred prior to the 30 silicate treatment in order to keep it free of contaminants from the first stage(s). Aqueous silicate sols are generally stable at very high concentrations provided the pH is maintained, generally, above 10.0 and the solution is kept free of ionic contaminants. The components of the first 35 treatment stage will and do (at the surface - silicate

-9-

solution interface) induce polymerization leading to an [SiO<sub>2</sub>]<sub>x</sub> matrix. It is by this mechanism, along with the "substrate-O-[Group IV Metal]-O-Si-[SiO<sub>2</sub>]<sub>x</sub>" production, that the final coating is obtained and, therefore, it is desirable  
5 to keep the silicate solutions free of any contamination.

More particularly describing stage 1, the acidic, aqueous coating solution composition can be prepared from a variety of acids and salts which contain group IV-B metals, specifically Zr, Hf, or Ti. Fluoride may be added by the  
10 complex metal fluoride of the Group IVB metal, as an acid or salt of such a complex fluoride, by the many simple fluoride salts. Examples include KF, NaF, etc., acid fluorides such as HF, and preferably as H<sub>2</sub>ZrF<sub>6</sub> and KF. The essential acid component may be added from the acid metal (Group IV- B)  
15 fluoride or other mineral acids such as HNO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub>, HF, etc., and preferably as HNO<sub>3</sub>.

In one embodiment the invention incorporates Group IV-B metals (zirconium in the examples below) in solution with Group II-A metals (calcium in the examples below) at pH  
20 levels of 1.5 to 4.5 for the first treatment stage.

Dependent on concentration of the Group II-A and IV-B metals (generally, the higher level of metal concentration necessitates lower pH levels and, with increasing levels of metal and acid, a heavier coating is obtained) and fluoride  
25 in a mole ratio to Group IV-B and dissolved metal (e.g., aluminum) of at least 4 moles fluoride to each mole of metal. Fluoride must be balanced to maintain the working solution such that the metals remain soluble while little or no etching of the substrate occurs. This is dependent on  
30 acid and metal concentrations as the fluoride will move from the higher order metal fluorides to the lower order and preferentially to the metallic (oxide) surface. A small amount of etching of an oxide surface is acceptable, but much of the metal oxide resident on the surface prior to coating  
35 is maintained and gives additional protection in a corrosive

-10-

environment. Temperature of the working solution can range from 70°F to 180°F with 120 to 140°F being preferred. The surface so obtained is ready for the next stage of the process.

5 By example, acceptable coatings can be formed from solutions containing from 0.00015 M to 0.055 M, Group IV-B metal, with 0.00025 M to 0.03 Group II-A metal in Stage 1. The best ratio of Group IV-B to Group II-A metal will be dependent on the method of coating solution contact (spray, 10 dip, etc.), the working bath temperature, pH, and fluoride concentration.

In one aspect of the invention, Stage 1 comprises a 5 minute immersion at a temperature of 140°F, with concentrations of 150 to 600 ppm Zr, 80 ppm Ca, and 200 to 15 740 ppm F at a pH from 2.4 to 2.8. This embodiment of the invention gives superior corrosion protection when used in conjunction with Stage 2.

Working solutions can be made up to the solubility limits of the components in Stage 1 in combination to provide 20 acceptable coatings, but lower levels as described above are preferred, as dissolved substrate metal ions entering the coating solution during processing may cause precipitation of bath components in saturated and near saturated solutions. This can also be dealt with in the solutions disclosed so far 25 by other methods. For example, addition of a chelant such as Versenex 80 to a bath for treatment of ferrous substrate will yield a soluble ion complex with dissolved  $\text{Fe}^{x+}$ , extending the life and efficiency of the working solution. It should be noted that the presence of iron in working solutions for 30 aluminum and other metals may decrease the corrosion protection obtained. A chelant such as EDTA, triethanolamine, or Versenex 80 will preferentially complex the iron in solution and inhibit its incorporation into the conversion coatings for aluminum or magnesium.

35 Additionally, insoluble calcium salts which may form in

-11-

the higher temperature range mentioned may be more soluble at the lower temperatures and, therefore, the working solution should be used at the lower end of the temperature range when the calcium content of the working solution is at the high 5 end of the levels stated. Also, addition of a tripolyphosphate (as Na<sub>5</sub>P<sub>3</sub>O<sub>10</sub> or other polyphosphate salt) will assist in maintaining high levels of calcium in the treatment bath.

Addition of boron in the form of boric acid, borate 10 salts, or fluoroborates to the working solution has been shown to improve certain properties of the coatings obtained as described. The preferred range for boron is 50 to 100 ppm, typically present at 10 to 200 ppm.

Addition of phosphate to the working bath can add to 15 corrosion protection and paint adhesion to the coating obtained. It is commonly believed that the incorporation of phosphate into certain conversion coatings enhances protection from "pitting" corrosion; as when a pit is initiated in a corrosive environment, the phosphate present 20 will first dissolve into the pit area and, there, form insoluble salts with base (substrate) metal ions or other coating components, effectively sealing the pit.

Addition of zinc to the working solution has been shown 25 to produce coatings with improved corrosion resistance on ferrous substrates. It is believed the zinc accelerates coating deposition and, when incorporated into the coating (if reduced) may provide galvanic protection to the metal substrate. The typical range for zinc is 5 to 100 ppm, preferably 10 to 30 ppm.

30 Aluminum added to the working solution increases the rate of deposition of insoluble salts in the coating. Aluminum may be added in any form of soluble aluminum salt, preferably as a hydrated aluminum nitrate. Typically, aluminum may be present at 50 to 1,000 ppm, preferably at 100 to 200 ppm.

35 Working solutions composed of mixture(s) of the above

-12-

components may be applied by spray or dip coat applications. After the coating in the first stage has formed the surface should be rinsed with clean water. The rinse(s) may be deionized or tap water and should remove any soluble salts  
5 which might be present on the surface.

The first stage is generally monitored by a simple acid-base titration and pH. A 10 or 100 mL bath sample is taken (whichever is desired for accuracy and convenience - a 100 mL sample gives the more accurate result) and titrated to 10 methyl orange ( $/\text{pH} = 4.5$ ) with 0.10 N NaOH. This measure tells the available "free acid" in the bath and is used in conjunction with the pH measurement. The same or other (equivalent size) bath sample is titrated to phenolphthalein ( $/\text{pH} = 8.5$ ). This measure gives the Group IV-B available to 15 enter into the surface coating. When aluminum or other "metal hydroxide" forming element is present in solution (such as when aluminum evaporators are being processed) it must be considered that this will add to this titration value. This can be dealt with (if deemed necessary) by use 20 of complexants, excess fluoride addition during titration, or multiple indicator systems if deemed necessary. We have found that for coating aluminum evaporators, the titration of 100 mL of this bath against 17.0  $\pm$  5.0 mL 0.10 N NaOH provides excellent results, as when the "free acid" is 25 maintained by concentrate addition aluminum reaches a steady-state concentration and an equilibrium between dissolution/deposition develops.

#### STAGE 2

Stage 2 is comprised of a stable aqueous solution of, 30 preferably, at least 5 percent by weight sodium silicate (eg., Grade 42 sodium silicate) in water. The silicate may be any stable silicate sol but sodium silicate will be used for this discussion. It has been seen that the odor impact

-13-

of the surface is reduced as the concentration of the silicate is increased, reaching a minimum above 5 percent w/w as sodium silicate.

The temperature of this stage can range from ambient  
5 (about 70°F) up to about 180°F. The preferred range is 90°F to 120°F, 110°F being most preferred at a 10% sodium silicate concentration.

Superior corrosion protection is obtained when the silicate concentration is at least 2% w/w. This parameter  
10 can depend on the exact nature of the prior stage(s) and, due to all considerations, a 10% w/w solution maintained at a pH of 11.1 +/- 0.5 is recommended for optimal performance in heat exchanger applications.

As stated above, gelation of this stage can occur if the  
15 pH becomes too low and/or a high level of contamination is experienced. It must be cautioned here as well that the alkalinity must not be excessive so as not to attack the layer provided in Stage 1 above (or other prior supplemental stages) and then the substrate itself. This, of course,  
20 becomes more pronounced in the higher end of the recommended temperature range.

The control for stage 2 is done by monitoring of pH (kept in the range stated above) and a simple acid-base titration. For titration, five milliliters of bath solution are taken,  
25 diluted to approximately 50 mL with deionized or distilled water, and titrated with 0.10 N HCl to phenolphthalein (/pH = 8.5). When Grade #42 sodium silicate is used, the equation:

$$[0.5 \times \text{mL } 0.10 \text{ N HCl} = \% \text{ silicate}]$$

can be used. A graph of mL acid versus % #42 silicate can  
30 also be used, with 0.5 being the approximate slope of the line. More specific measures of the  $\text{Na}_2\text{O}/\text{SiO}_2$  ratio can also be used, but have not been necessary in preferred embodiments to date.

Additionally, the second stage as described here may be  
35 augmented for reduction in solids formation by maintaining a

-14-

proper concentration of chelant in the solution. A wide variety of chelants will complex hard water minerals and metals from prior stage(s) which will reduce the formation of insoluble Group IIA [or other] silicate salts. Several 5 classes of chelants have been found to be effective to a substantial extent: tripolyphosphates (such as Na<sub>2</sub>P<sub>2</sub>O<sub>5</sub>, trisodium phosphate, KTPP potassium pyrophosphate), phosphonates (such as Dequest 2000, 2010, 2060), EDTA and Versene 120, sodium gluconates, and borax. 10 This augmentation may allow the manufacturing process to achieve greater production quantities through this stage before dumping and recharging becomes necessary. Indications are that silicate scale build up on racks and equipment surfaces that come into intermittent contact with the 15 solution may be reduced, as well.

It must be cautioned that high concentrations of chelant(s) may affect with the oxide matrix that forms in Stage 2 and change characteristics of the coating. The benefits to the manufacturing process must be balanced with 20 the desired characteristics of the coating in each particular case.

### STAGE 3

Stage 3 is the "drying" stage and is the point in the process where the coating composition becomes "fixed." There 25 is no augmentation of the coating after this point other than to paint over it, which may require a "pre-paint treatment" to enhance adhesion. This stage is generally at an elevated temperature for a duration long enough to complete the formation of covalent mixed metal oxide linkages. A gradual 30 increase in surface and part temperature, as moisture will be leaving the coating as linkages form and as the aqueous portion of the residual coating solutions evaporates, is preferred. The peak surface temperature should be from 200

-15-

to 450°F, 250 to 275°F being preferred in the described embodiment. The temperature of the coated surface should remain at the drying temperature for at least 5 minutes to ensure completion of the "drying" reactions and eventual 5 evaporation of all water associated with the surface.

Extended periods at elevated temperatures should be avoided, as should rapid descents in temperature (such as that experienced in quenching operations). The coating is considered to be an amorphous mixed metal oxide/siloxyl type 10 and will normally have a different coefficient of thermal expansion/contraction than the substrate and, therefore, excessively rapid or extreme temperature fluctuations are to be avoided in this stage.

In the preferred embodiment for typical air conditioning 15 evaporators for automobiles, it has been determined that, in general, 15 minutes at 300°F yields a satisfactory coating with regard to the described desired characteristics. This parameter has been tested for many sizes and models (as have the other stages) and the stated values work well in ovens 20 where there is some circulation of heated air through the parts.

As with most chemical treatment operations, automatic controls may be used to add chemical concentrates to the treatment stages during processing with the described 25 process. Conductivity or pH regulation of the feed pumps is used to keep the Stage 1 and Stage 2 concentrations in the desired ranges. Once the first two stages have reached a stable "steady" state with regard to the specified pH and titration values for a given operation, the conductivity (or 30 pH) control is set to feed concentrate to maintain the value in the treatment stage. The "steady" state is reached when reaction product (such as Al<sup>3+</sup>) has built up in the stages to its peak level. This state can be reached in a new bath by addition of a "charge supplement" of the known reaction 35 product(s) at their steady-state levels.

-16-

Reference will now be made to specific examples using the processes described above. It is to be understood that the examples are provided to more completely describe preferred embodiments, and that no limitation to the scope of the invention is intended thereby.

5

#### EXAMPLE 1

A first solution containing 150 ppm Zr and 200 ppm F at a pH of 2.4 is prepared and the solution is maintained at a temperature of about 140°F. An air conditioning heat exchanger is immersed in the first solution for five minutes.

10

A second solution of about 2% silicate, at a pH of about 10, is prepared and maintained at a temperature of about 90°F. The heat exchanger which has been immersed in the first solution above is subsequently immersed in the second solution.

15

The treated heat exchanger is dried in an oven for one hour to produce a low-odor, bioresistant, hydrophilic, corrosion resistant coating.

#### EXAMPLE 2

20 A first solution containing 600 ppm Zr and 750 ppm F at a pH of 2.8 is prepared and the solution is maintained at a temperature of about 140°F. An air conditioning heat exchanger is immersed in the first solution for five minutes.

25

A second solution of about 10% silicate, at a pH of about 12, is prepared and maintained at a temperature of about 90°F. The heat exchanger which has been immersed in the first solution above is subsequently immersed in the second solution.

The treated heat exchanger is dried in an oven for one

-17-

hour to produce a low-odor, bioresistant, hydrophilic, corrosion resistant coating.

#### EXAMPLE 3

A first solution containing 150 ppm Zr, 80 ppm Ca and 200  
5 ppm F at a pH of 1.5 is prepared and the solution is maintained at a temperature of about 140°F. An air conditioning heat exchanger is immersed in the first solution for five minutes.

A second solution of about 2% silicate, at a pH of about  
10, 10, is prepared and maintained at a temperature of about 90°F. The heat exchanger which has been immersed in the first solution above is subsequently immersed in the second solution.

The treated heat exchanger is dried in an oven for one  
15 hour to produce a low-odor, bioresistant, hydrophilic, corrosion resistant coating.

#### EXAMPLE 4

A first solution containing 600 ppm Zr, 80 ppm Ca and 740  
ppm F at a pH of 4.5 is prepared and the solution is  
20 maintained at a temperature of about 140°F. An air conditioning heat exchanger is immersed in the first solution for five minutes.

A second solution of about 10% silicate, at a pH of about 12, is prepared and maintained at a temperature of about  
25 90°F. The heat exchanger which has been immersed in the first solution above is subsequently immersed in the second solution.

The treated heat exchanger is dried in an oven for one  
hour to produce a low-odor, bioresistant, hydrophilic,  
30 corrosion resistant coating.

-18-

EXAMPLES 5-8

Further samples were treated as described in Examples 1-4 above, but also including the additional steps of rinsing the metal with deionized water after each immersion step. After 5 drying, the treated heat exchangers had a low-odor, bioresistant, hydrophilic, corrosion resistant coating.

EXAMPLE 9

A first solution containing 0.00015 M Zr, 0.00025 M Ca and 200 ppm F at a pH of 1.5 is prepared and the solution is 10 maintained at a temperature of about 140°F. An air conditioning heat exchanger is immersed in the first solution for five minutes.

A second solution of about 2% silicate, at a pH of about 10, is prepared and maintained at a temperature of about 15 90°F. The heat exchanger which has been immersed in the first solution above is subsequently immersed in the second solution.

The treated heat exchanger is dried in an oven for one hour to produce a low-odor, bioresistant, hydrophilic, 20 corrosion resistant coating.

EXAMPLE 10

A first solution containing 0.055 M Zr, 0.00025 M Ca and 740 ppm F at a pH of 4.5 is prepared and the solution is maintained at a temperature of about 140°F. An air 25 conditioning heat exchanger is immersed in the first solution for five minutes.

A second solution of about 10% silicate, at a pH of about 12, is prepared and maintained at a temperature of about 90°F. The heat exchanger which has been immersed in the 30 first solution above is subsequently immersed in the second solution.

-19-

The treated heat exchanger is dried in an oven for one hour to produce a low-odor, bioresistant, hydrophilic, corrosion resistant coating.

#### EXAMPLE 11

5       A first solution containing 0.00015 M Ti, 0.00025 M Ca and 200 ppm F at a pH of 2.0 is prepared and the solution is maintained at a temperature of about 140°F. An air conditioning heat exchanger is immersed in the first solution for five minutes.

10      A second solution of about 5% silicate, at a pH of about 11, is prepared and maintained at a temperature of about 90°F. The heat exchanger which has been immersed in the first solution above is subsequently immersed in the second solution.

15      The treated heat exchanger is dried in an oven for one hour to produce a low-odor, bioresistant, hydrophilic, corrosion resistant coating.

#### EXAMPLE 12

A first solution containing 0.055 M Ti, 0.00025 M Ca and 20 740 ppm F at a pH of 2.5 is prepared and the solution is maintained at a temperature of about 140°F. An air conditioning heat exchanger is immersed in the first solution for five minutes.

A second solution of about 10% silicate, at a pH of about 25 12, is prepared and maintained at a temperature of about 90°F. The heat exchanger which has been immersed in the first solution above is subsequently immersed in the second solution.

The treated heat exchanger is dried in an oven for one 30 hour to produce a low-odor, bioresistant, hydrophilic, corrosion resistant coating.

-20-

While the invention has been illustrated and described in detail in the foregoing description, the same is to be considered as illustrative and not restrictive in character, it being understood that only the preferred embodiment has 5 been shown and described and that all changes and modifications that come within the spirit of the invention are desired to be protected.

-21-

CLAIMS

What is claimed is:

1. A process for providing an "odorless" corrosion coating to metal surfaces, the process comprising:

5 (a) treating a metal surface with a first solution comprising:

- (i) fluoride;
- (ii) a group II-A metal;
- (iii) zirconium and

10 (iv) a protic acid;

(b) subsequently treating said metal surface with a second solution comprising water-soluble silicate at an alkaline pH; and

(c) drying the metal surface.

15 2. A process according to claim 1 wherein each of said treating steps is accomplished by immersing the metal surface in a bath.

20 3. A process according to claim 1 wherein each of said treating steps is accomplished by spraying the metal surface with a solution.

4. A process according to claim 1 and further including the step of rinsing the metal surface before treating it with said second solution.

25 5. A process according to claim 1 and further including the step of rinsing the metal surface after treating it with said second solution.

6. A process according to claim 1 and further including the step of pretreating the metal surface by etching the oxide or by heavy deposition of a Group IV-B salts.

-22-

7. A process according to claim 1 and further including the step of pretreating the metal surface with a solution comprising a Group IV-B metal and a Group II-A metal.

8. A process according to claim 1 wherein said second  
5 solution comprises a soluble sodium silicate or a soluble potassium silicate.

9. A process according to claim 1 wherein said first solution is at a pH of between about 1.5 and about 4.5.

10. A process according to claim 1 wherein said first  
10 solution comprises between about 0.00015 M and 0.055 M Group IV-B metal, and between about 0.00025 M and 0.03 M Group II-A metal.

11. A process according to claim 1 wherein said first solution comprises between about 150 ppm and about 600 ppm  
15 Group IV-B metal, about 80 ppm Ca, and between about 200 ppm and about 740 ppm F<sup>-</sup>.

12. A process according to claim 1 wherein said first solution has a temperature of about 140°F.

13. A process according to claim 1 wherein said first  
20 solution has a pH of between about 2.4 and about 2.8.

14. A process according to claim 1 wherein said second solution comprises at least 2% w/w silicate.

15. A process according to claim 14 wherein said second solution comprises about 10% w/w silicate.

25 16. A process according to claim 15 wherein said second solution is at a pH of between about 10 and 12.

-23-

17. A process for providing an "odorless" corrosion coating to metal surfaces, the process comprising:

(a) treating a metal surface with a first solution comprising:

5 (i) fluoride;

(ii) a Group IV-B metal selected from the group consisting of zirconium, halfnium and titanium;

(iii) a protic acid; and

(iv) a group II-A metal;

10 (b) subsequently treating said metal surface with a second solution comprising water-soluble silicate at an alkaline pH; and

(c) drying the metal surface.

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/US96/00517

**A. CLASSIFICATION OF SUBJECT MATTER**

IPC(6) :C23C 22/34

US CL :148/247

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 148/247

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y,P	US, A, 5,380,374 (TOMLINSON) 10 January 1995, col. 2, lines 25 -33 and col. 5, lines 35-40.	1-17
Y	US, A, 4,462,842 (UCHIYAMA ET AL) 31 January 1984, col. 2, lines 7-50	1-17

Further documents are listed in the continuation of Box C.  See patent family annex.

• Special categories of cited documents:	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
*A* document defining the general state of the art which is not considered to be of particular relevance	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
*E* earlier document published on or after the international filing date	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
*L* document which may throw doubt on priority claim(s) or which is cited to establish the publication date of another citation or other special reasons (as specified)	"&"	document member of the same patent family
*O* document referring to an oral disclosure, use, exhibition or other means		
*P* document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search

03 APRIL 1996

Date of mailing of the international search report

21 MAY 1996

Name and mailing address of the ISA/US  
Commissioner of Patents and Trademarks  
Box PCT  
Washington, D.C. 20231

Facsimile No. (703) 305-3230

Authorized officer

SAM SILVERBERG

Telephone No. (703) 305-9646

Form PCT/ISA/210 (second sheet)(July 1992)\*